

## SHORT COMMUNICATIONS

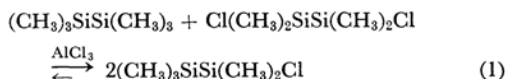
# Aluminum Chloride-Catalyzed Reactions of Organosilicon Compounds. A Rapid Redistribution Reaction of Chlorodisilanes

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In recent years, considerable attention has been directed toward a study of the organopolysilanes.<sup>1,2</sup> An interesting example of this involves the reaction of organodisilanes with an electrophilic reagent.<sup>2</sup> During the course of an investigation of the reactivity of organopolysilanes toward electrophiles, we have found that methylchlorodisilanes readily undergo aluminum chloride-catalyzed redistribution reaction at room temperature, while the disproportionation of alkylchlorosilanes catalyzed by aluminum chloride has been reported to proceed slowly, even at much higher temperatures.<sup>3,4</sup>



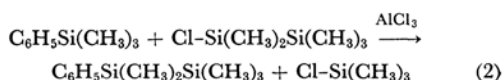
When an equimolar mixture of hexamethyldisilane and 1,2-dichlorotetramethyldisilane is stirred at room temperature in the presence of anhydrous aluminum chloride (0.05–0.25 mol./l.), the equilibrium is established between pentamethylchlorodisilane and its original components within 1.5 hr.<sup>5</sup>

As the equilibrium is established rapidly in favor of pentamethylchlorodisilane, the reaction can be applied in a preparative scale. In a typical ex-

periment a mixture of 73.5 g. of hexamethyldisilane, 94.5 g. of tetramethyldichlorodisilane, and 5.5 g. of anhydrous aluminum chloride was stirred for about 2 hr. at room temperature. After 3 g. of acetone had been added to the mixture to deactivate the catalyst, the mixture was subjected to simple distillation under reduced pressure. The fractionation of the distillate gave 114 g. (68.5%) of pure pentamethylchlorodisilane.

In view of these findings, it became of interest to investigate the aromatic substitution by a mixture of pentamethylchlorodisilane and aluminum chloride, since it is well known that halosilanes do not react with benzene in the presence of Lewis acid.<sup>3,4</sup>

Although an attempted silylation of benzene by a mixture of pentamethylchlorodisilane and aluminum chloride was unsuccessful, we have found that detrimethylsilylation was effected very rapidly by pentamethylchlorodisilane in the presence of a catalytic amount of aluminum chloride.



Using competitive reaction conditions in benzene, we found that phenyltrimethylsilane underwent the reaction faster than *p*-chlorophenyltrimethylsilane and slower than *p*-methylphenyltrimethylsilane with pentamethylchlorodisilane.<sup>6</sup>

The order of substituent effects demonstrates the electrophilic nature of the reaction; it also confirms the present reaction to be a new class of aromatic electrophilic substitution.<sup>7</sup>

6) The apparent relative rates at an early stage of the reaction were found:  $k_{p\text{-CH}_3}/k_{\text{H}}=2.0$  and  $k_{p\text{-Cl}}/k_{\text{H}}=0.2$ .

7) R. O. C. Norman and R. Taylor, "Electrophilic Substitution in Benzenoid Compounds," Elsevier Publishing Co., Amsterdam (1965).

1) C. Eaborn, "Organosilicon Compounds," Butterworths Scientific Publications, London (1960), p. 351.

2) H. Sakurai, T. Imoto, N. Hayashi and M. Kumada, *J. Am. Chem. Soc.*, **87**, 4001 (1965).

3) H. Gilman and G. E. Dunn, *Chem. Revs.*, **52**, 77 (1953).

4) G. A. Russell, *J. Am. Chem. Soc.*, **81**, 4831 (1959), and references therein.

5) The apparent equilibrium constant,  $K=[\text{C}_6\text{H}_5\text{Si}(\text{CH}_3)_2\text{Si}(\text{CH}_3)_3]/[\text{C}_6\text{H}_5\text{Si}(\text{CH}_3)_3][\text{C}_6\text{H}_5\text{Si}(\text{CH}_3)_2\text{Si}(\text{CH}_3)_2\text{Cl}]$ , was found to be 82.6 for the original mixture of 6.22 mmol. of hexamethyldisilane, 5.78 mmol. of tetramethyldichlorodisilane and 1 mmol. of aluminum chloride in 20 ml. of benzene. In chloroform, however, the reaction did not proceed even after one week at room temperature.